

DOCKET NO: 287263UD0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
VOLKER HENNIGE : EXAMINER: ZACHARY P. BEST
SERIAL NO: 10/575,759 :
FILED: APRIL 13, 2006 : GROUP ART UNIT: 1795
FOR: ELECTRIC SEPARATOR :
COMPRISING A SHUTDOWN
MECHANISM, METHOD FOR THE
PRODUCTION THEREOF, AND USE IN
LITHIUM BATTERIES

APPEAL BRIEF

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

This is an appeal from the Second Rejection dated October 17, 2008. A Notice of Appeal was timely filed on March 10, 2009.

I. REAL PARTY IN INTEREST

The real party in interest in this appeal is Degussa AG, having an address of Bennigsenplatz 1, D-40474 Düsseldorf, Germany.

II. RELATED APPEALS AND INTERFERENCES

Appellants, Appellants' legal representative and the assignee are aware of no appeals, interferences, or judicial proceedings which may be related to, directly affect or be directly affected by or have a bearing on the Board's decision in this appeal.

III. STATUS OF THE CLAIMS

Claims 2-9 and 12-26 stand rejected and are herein appealed. Claims 1 and 10-11 are canceled.

IV. STATUS OF THE AMENDMENTS

An amendment under 37 CFR 1.116 filed, January 16, 2009, is entered to the record for purposes of appeal.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

It is preliminarily noted that references in brackets are to page and line number of the specification as filed.

Independent Claim 25 is directed to an electrical separator for a lithium battery which will shut down ion flow between the electrodes and lead to battery cell shutdown in the event of battery dysfunction. The electrical separator is a thin porous insulating material which is pervious to ions [page 1, lines 11-14]. Appellants have described that the claimed electrical separator is not electroconductive because electroconductivity could impart internal short circuiting in the lithium battery [page 2, lines 20-25].

The claimed electrical separator contains a porous nonelectroconductive carrier [page 2, lines 24-25] which is coated with a porous nonelectroconductive inorganic material which

in turn, supports a shutdown layer which will melt at the shutdown temperature of the battery. The shutdown layer is composed of materials which have a defined melting point [page 4, lines 21-22][page 18, line 30] and therefore melts at the shutdown temperature of the separator [page 4, lines 8-11].

The porous nonelectroconductive carrier has a porosity greater than 50% [page 6, lines 13-16] where porosity describes the amount of accessible, open pores [page 9, lines 1-2]. The carrier is coated on and in the pores with an inorganic coating [page 10, lines 6-9] which comprises particles of Al, Si and/or Zr oxides having particle sizes in the range from 0.5 to 10 μm [page 7, lines 11-13]. The particles are applied to the carrier as a suspension in a sol of Al, Zr and/or Si [page 10, lines 24-26] and the sol is then solidified [page 15, lines 15-17].

Claims 2-9, 12-24 and 26 depend directly or indirectly from Claim 25 and stand or fall with the independent claim.

There is no means plus function or step plus function description under 35 U.S.C. 112, sixth paragraph in the claims of this application.

VI. REJECTIONS TO BE REVIEWED ON APPEAL

Ground (A)

Claims 2-9 and 12-26 stand rejected under 35 U.S.C. § 112, first paragraph, as failing to comply with the written description requirement.

Ground (B)

Claims 2-9 and 12-26 stand rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Ground (C)

Claims 2-9 and 12-26 stand rejected under 35 U.S.C. § 103(a) for obviousness over Shi et al. (U.S. 2005/0014063) in view of Hying et al. (WO99/62620, equivalent to U.S. 6,620,320) and Takita et al. (U.S. 5,922,492).

VII. ARGUMENT

Ground (A)

Rejection under 35 U.S.C. §112, first paragraph, as failing to comply with the written description requirement.

Claims 2-9 and 12-26

Claim 25 recites that:

. . . in the porous inorganic nonelectroconductive coating the particles are adhered together by an oxide of Al, Si or Zr, . . .

The Examiner has stated (Official Action dated October 17, 2008, page 3, Issue 7, second paragraph):

However, it is noted that in the instant specification adherence together by oxides of only Zr or Si are discussed . . . It is noted that Applicant alleges support for adherence by an oxide of aluminum can be found in the instant specification . . . However, the intended support discusses only suspending oxide particles of Al, Si, and/or Zr in a sol of Al, Zr[Si], and/or Zr. No discussion is given regarding adherence by an oxide of aluminum.

Appellants previously pointed to description in the specification in support of the formation of an Aluminum oxide material adhering the claimed oxidic particles (Reply to Official Action dated October 17, 2008, filed January 16, 2009, page 12, lines 3-11). The Examiner erroneously continues to be of the opinion that because the specification does not

specifically state adherence by aluminum oxide, the language of Claim 25 is not supported (Advisory Action dated February 19, 2009, Continuation Sheet, second paragraph).

The M.P.E.P. § 2163 B. states:

While there is no *in haec verba* requirement, newly added claim limitations must be supported in the specification through express, implicit, or inherent disclosure.

Citing *Wang Labs. v. Toshiba Corp.* (993 F. 2d 858, 865, 26 USPQ2d 1767,1774

(Fed. Cir. 1993)) the M.P.E.P. 2163 II. 2. further states:

The analysis of whether the specification complies with the written description requirement calls for the examiner to compare the scope of the claim with the scope of the description to determine whether applicant has possession of the claimed invention. Such a review is conducted from the standpoint of one of skill in the art at the time the application was filed . . . and should include a determination of the field of the invention and the level of skill and knowledge in the art. . . . Information which is well known in the art need not be described in detail in the specification.

Appellants have described in the specification as filed, the following:

The suspension used for producing the coating comprises at least one oxide of aluminum, of silicon and/or of zirconium and at least one sol of the elements Al, Zr and/or Si and is prepared by suspending particles of at least one oxide in at least one of these sols. (page 10, lines 24-26)

The sols are obtained by hydrolyzing at least one compound of the elements Zr, Al and/or Si. (page 10, line 30)

The suspension present on and in the carrier as a result of the coatings can be solidified for example by heating at from 50 to 350°C. Since the maximum temperature is dictated by the carrier material when polymeric substrate materials are used, the maximum temperature must be adapted accordingly. Thus, depending upon the embodiment of the process, the suspension present on and in the carrier is solidified by heating at from 100 to 350°C and most preferably by heating at from 200 to 280°C. It can be advantageous for the heating to take place at from 150 to 350°C for from 1 second to 60 minutes. It is more preferable to solidify the suspension by heating at from 110 to 300°C and most preferably at from 200 to 280°C and preferably for from 0.5 to 10 min. The assembly may be heated by means of heated air, hot air, infrared radiation or by other heating methods according to the prior art. (page 15, lines 12-21)

Appellants respectfully submit that based on the above specification text, one of ordinary skill in the art would recognize that the application as filed, clearly describes a sol of aluminum oxide containing suspended oxidic particles is applied to the carrier and solidified to obtain a coating having particles adhered together by an oxide of aluminum. Appellants support their position that such technology is known to one of ordinary skill in the art as exemplified by the attached excerpt from a chapter in Kirk-Othmer, entitled Sol-Gel Technology (Kirk-Othmer Encyclopedia of Chemical Technology, Fifth Edition, Vol. 23, pages 76-79). Alumina-oxide films prepared by a sol-gel method is described therein. Appellants respectfully request that judicial notice of this reference be taken. (*In re Raynes*, 7 F3d. 1037, 28 USPQ2d 1630) Appellants submit that as the oxidic particles are suspended in the sol, when the sol is solidified, the particles are adhered by the solidified alumina oxide film. The same procedure is followed for sols of Si and Zr and therefore the Examiner has not explained why the case with Al would be different.

For all the above reasons, the rejection of Claims 2-9 and 12-26 under 35 U.S.C. §112, first paragraph, should be reversed.

Ground (B)

Rejection under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Claims 2-9 and 12-26

Claim 25 states that:

. . . the shutdown layer will melt at a temperature determined as the shutdown temperature of the electrical separator.

The Examiner has stated (Official Action dated October 17, 2008, page 4, Issue 8, second paragraph):

However, no relation is given as to how “the shutdown temperature of the electrical separator” is defined. Furthermore, if the shutdown layer causes the shutdown of the separator then the shutdown temperature will be the temperature at which the shutdown layer melts resulting in circular and indefinite characterization.

Appellants have described that:

These separators according to the present invention comprise a shutdown mechanism which is based on the shutdown layer melting at a predetermined temperature and closing the separator by the material of the shutdown layer penetrating into the pores of the inorganic material and closing them. The separator according to the present invention can never melt down, since the inorganic layer prevents large-area short circuiting within the battery even at higher temperatures. **The separators according to the present invention thus meet the demands of various battery manufacturers for a safety shutdown within the battery cells.** The inorganic particles ensure that there can never be a meltdown. It is accordingly ensured that there are no operating states that give rise to large-area short circuiting. (Bold added) (page 4, lines 8-16)

The shutdown layer which, according to the present invention, is present on the inorganic layer can consist for example of natural or artificial waxes, (low-melting) polymers, for example specific polyolefins, for example polyethylene or polypropylene, or polymer blends or mixtures, in which case **the material for the shutdown layer is selected so that the shutdown layer will melt at the desired shutdown temperature** and close the pores of the separator, substantially preventing any further ion flux. (Bold added) (page 8, lines 3-8)

Appellants have indicated that one advantage of the claimed separator is the high degree of safety obtained by having a shutdown effect, with no meltdown occurring. (page 5, line 16) As indicated by the above description, a shutdown temperature may be specified by a battery manufacturer and the electrical separator according to the claimed invention can be constructed by proper choice of shutdown layer composition to have a melting point meeting the battery manufacturer's desired or specified shutdown temperature.

Definiteness under 35 U.S.C. § 112, second paragraph, is determined by whether “those skilled in the art would understand what is claimed when the claim is read in light of the specification.” *Orthokinetics, Inc. v. Safety Travel Chairs, Inc.*, 806 F.2d 1565,1576, 1 USPQ2d 1081,1088 (Fed. Cir. 1986). Appellants submit that one of ordinary skill in the art would recognize that the composition of the shutdown layer can be adjusted to have a melting temperature at a specific shutdown temperature which is determined by the design and components of the battery as well as the required safety designed into the battery by a manufacturer.

Therefore, contrary to the Examiner’s erroneous assertion, Appellants have described how the shutdown temperature is determined and how the composition of the shutdown layer is selected to obtain a melting point meeting the requirement of the shutdown temperature. Moreover, Appellants contend that one of ordinary skill in the art would recognize and understand the relationship.

In view of the foregoing, the rejection of Claims 2-9 and 12-26 under 35 U.S.C. §112, first paragraph, should be reversed.

Ground C

Rejection under 35 U.S.C. § 103(a) for obviousness over Shi et al. (U.S. 2005/0014063) in view of Hying et al. (WO99/62620, equivalent to U.S. 6,620,320) and Takita et al. (U.S. 5,922,492).

Claims 2-9 and 12-26

Shi describes a battery separator having a nonwoven flat sheet, a microporous membrane having low temperature shutdown properties and an adhesive bonding the nonwoven flat sheet to the microporous membrane which is adapted for swelling when

contacted by an electrolyte. (Claim 1) The nonwoven and/or its fibers may be coated or surface treated with ceramic material [0014].

Hying describes ion-conducting composites for chemical and physical processes such as electrodialysis, electrolysis and chemical catalysis. The composite material contains ionic groups such as sulfonic acids, phosphoric acids, carboxylic acids to impart ion conductivity to the membrane (Claim 1). Such groups are described as ionogenic groups and the presence of these groups on and in the composite leads to ion conduction by a surface diffusion method (Col. 2, lines 15-17).

Hying states (Col. 2, lines 22-24):

“Not only good conductivity but also the greatest possible permselectivity is necessary for use of membranes in electrodialysis or as a proton-conducting membrane in fuel cells.”

Hying further describes that the (Col. 2, lines 33-40):

... permeable composite material according to the invention based on at least one porous and permeable support, which on at least one side of the support and on the interior of the support is provided with at least one inorganic component, which substantially contains at least one compound of a metal, a semi-metal or a mixed metal with at least one element of Group 3 to Group 7, exhibits ion-conducting properties.

Appellants have previously argued that Shi and Hying are directed to unrelated technologies and cannot be combined (Reply to Official Action dated October 17, 2008, filed January 16, 2009, page 10, line 7 bridging to page 11, line 5) and that such combination would render Shi unsatisfactory for its intended use or change its principle of operation (MPEP 2143.01 V. and VI.) (Reply to Official Action dated October 17, 2008, filed January 16, 2009, page 11, lines 6-14). The Examiner has responded to Appellants arguments (Advisory Action dated February 19, 2009, Continuation Sheet, first paragraph) stating:

Examiner is not persuaded because both references apply to the transportation of ions through a separating medium. There is no teaching from either reference that a “surface diffusion mechanism” would destroy or alter the use of the separator of Shi et al. in a battery.

Appellants believe the Examiner is incorrect in both statements. Appellants have described a battery separator as (page 1, lines 11-13) as:

The separator is customarily a thin porous insulating material possessing high ion perviousness, good mechanical strength and long-term stability to the chemicals and solvents used in the system, for example in the electrolyte of the battery.

As recited in the specification and claims the separator is nonelectroconductive, but pervious to ions. This property is required for the separator to insulate the electrodes from one another while allowing ions to move from one electrode to another. If the perviousness is removed as when the shutdown layer melts and fills the pores, ion mobility between the electrodes is prevented. The microporous separator described by Shi provides a similar effect. In contrast, the ion-conducting composite describe by Hying incorporates ionogenic groups in and on the composite which provide sites for ion conduction. Ion conduction is known to one of ordinary skill in the art to occur via movement of ions from one ionogenic group to another across the composite material. The presence of such ionogenic groups therefore renders the composite electroconductive and a melt shutdown which enters the pores would not be effective to prevent ion mobility between electrodes across the composite.

The Examiner appears to recognize this basic principal by stating (Official Action dated October 17, 2008, page 5, lines 17-19):

The separator would be inherently nonelectroconductive because it could not function as a separator if it conducted electrons.

Appellants agree with the Examiner’s statement and add that the same is true regarding the conduction of ions other than electrons. Such conduction is exactly the

function of the Hying composite. Therefore, as Applicants have previously argued, adding the ionogenic groups described by Hying to the separator of Shi would render the Shi separator electroconductive and therefore unsatisfactory for its intended use or would change its principle of operation (MPEP 2143.01 V. and VI.)

Appellants also point out that the Examiner has cited Claim 22 of the reference and erroneously characterized the Hying coating as nonelectroconductive (Official Action dated October 17, 2008, page 6, lines 1-2). Claim 22 clearly recites that the composite material exhibits ion-conducting properties and contains at least one inorganic and/or organic material which exhibits ion-conducting properties. The coating cannot therefore be nonelectroconductive as erroneously alleged.

Takita describes a microporous polyolefin composite membrane comprising a microporous polyolefin membrane and a polyolefin nonwoven fabric laminated on at least one surface of the microporous polyolefin membrane. Takita does not disclose or suggest a porous inorganic nonelectroconductive coating and therefore, this reference does not provide a cure for the deficiency of the Shi/Hying combination described above.

Appellants also note that the Examiner has stated in his response to Applicant's arguments (Official Action dated October 17, 2008, page 9, lines 2-9):

Shi et al teach a battery separator, which must ionically conduct ions between the anode and cathode with which the separator separates . . . Therefore, the invention of Shi et al. would fall under the genus of the invention of Hying et al. of ion-conducting materials . . . Hying et al. directly mentions fuel cells (an electrochemical device similar to a battery) and more broadly mentions ion-conducting materials of its invention may be used for other electrochemical reactions . . . Therefore, one skilled in the art would have looked in the general field of ion-conducting materials to modify s subset of ion-conducting materials such as battery separators.

As Appellants have described, battery separators are pervious to ions and do not actively ion-conduct as described by Hying. The ionogenic groups required by Hying would render the microporous separator according to Shi electroconductive and therefore unsuited

to function as a battery separator. The uses described by Hying for the ion-conducting composite require active ion-conduction, including a fuel cell membrane. Contrary to the Examiner's statement a fuel cell and a battery are different technologies. Batteries are charged and discharged and store charged energy. A fuel cell operates only in the direction of energy generation and does not function to store electrical energy. Therefore, Appellants submit that one of ordinary skill in the art of battery separators which are not electroconductive would not look to the technology of ion-conducting membranes to obtain the claimed invention.


In view of all the above, the rejection of Claims 2-9 and 12-26 under 35 U.S.C. § 103(a) for obviousness over Shi et al. (U.S. 2005/0014063) in view of Hying et al. (WO99/62620, equivalent to U.S. 6,620,320) and Takita et al. (U.S. 5,922,492) should be reversed.

CONCLUSION

For the above reasons, it is respectfully requested that all outstanding rejections of the pending claims be reversed.

Respectfully submitted,

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VIII. CLAIMS APPENDIX

Claim 1 (Canceled).

Claim 2 (Rejected): The separator of claim 25,
wherein the shutdown layer is at least one selected from the group consisting of a
woven, a nonwoven, a felt, a formed-loop knit and a porous film.

Claim 3 (Rejected): The separator of claim 25, wherein
the separator is bendable down to a radius of 0.5 mm, and
the carrier is less than 50 μm in thickness.

Claim 4 (Rejected): The separator according to claim 3, wherein
the carrier is a nonwoven comprising polymeric fibers.

Claim 5 (Rejected): The separator of claim 25, wherein
the polymeric fibers of the carrier are selected from fibers of the group consisting of
polyacrylonitrile, polyester, polyamide and mixtures thereof.

Claim 6 (Rejected): The separator of claim 25, wherein
the shutdown layer is from 1 to 20 μm in thickness.

Claim 7 (Rejected): The separator of claim 25, wherein
the shutdown layer comprises at least one material selected from the group consisting
of polymers, polymer blends, natural or artificial waxes and mixtures thereof.

Claim 8 (Rejected): The separator of claim 25, wherein
the shutdown layer consists of a material which has a melting temperature of less than
130°C.

Claim 9 (Rejected): The separator of claim 25, wherein
the material of the shutdown layer and at least portions of the material of the carrier
are identical.

Claims 10-11 (Canceled).

Claim 12 (Rejected): The process of claim 26, further comprising
treating the porous inorganic nonconductive coating with a hydrophobicing agent
before fixing the porous sheet shutdown layer.

Claim 13 (Rejected): The process of claim 26, further comprising treating the porous
inorganic coating with an adhesion promoter before fixing the porous sheet shutdown layer.

Claim 14 (Rejected): The process according to claim 13,
wherein the sol is a polymeric sol comprising a silane adhesion promoter for the
shutdown layer to be applied later.

Claim 15 (Rejected): The process of claim 13,
wherein the adhesion promoter is a hydrolyzed or nonhydrolyzed functionalized
alkyltrialkoxysilane.

Claim 16 (Rejected): The process of claim 26,
wherein the porous sheet shutdown layer comprises a woven, formed-loop knit, felt, nonwoven or porous film.

Claim 17 (Rejected): The process of claim 13,
wherein fixing the porous sheet shutdown layer comprises
heating once to a temperature above 50°C and below the melting temperature of the material of the porous sheet shutdown layer so that the shutdown layer are adhered to the separator via the adhesion promoters.

Claim 18 (Rejected): The process of claim 26,
wherein fixing the porous sheet shutdown layer comprises
heating once to a temperature above the glass transition temperature of the porous sheet shutdown layer to incipiently melt the material without changing the actual shape.

Claim 19 (Rejected): The process of claim 26,
wherein fixing the porous sheet shutdown layer comprises
laminating the porous sheet shutdown layer to the porous inorganic nonelectroconductive coating.

Claim 20 (Rejected): The process of claim 26,
wherein fixing the porous sheet shutdown layer comprises applying the porous sheet shutdown layer to the porous inorganic nonelectroconductive coating and being trapped in a coil wound during battery fabrication.

Claim 21 (Rejected): The process of claim 26,
wherein
a material for the porous sheet shutdown layer is at least one selected from the group
consisting of polymers, polymer blends and natural and/or artificial waxes, and
the material has a melting temperature of less than 180°C.

Claim 22 (Rejected): The process according to claim 21,
wherein the porous sheet shutdown material is polyethylene.

Claim 23 (Rejected): A method for the production of a lithium battery comprising
employing the separator of claim 25 as a separator in the lithium battery.

Claim 24 (Rejected): A lithium battery comprising the separator of claim 25.

Claim 25 (Rejected): An electrical separator for a lithium battery comprising:
a porous carrier;
a porous inorganic nonelectroconductive coating on a surface and in the pores of the
porous carrier; and
a porous shutdown layer on the porous inorganic nonelectroconductive coating;
wherein
the porous carrier is nonelectroconductive and has a porosity greater than 50%,
the porous inorganic nonelectroconductive coating comprises particles of at least one
selected from the group consisting of an oxide of Al, an oxide of Si and an oxide of Zr, the
particles have an average particle size in the range from 0.5 to 10 µm, and in the porous

inorganic nonelectroconductive coating the particles are adhered together by an oxide of Al, Si or Zr, and

the porous shutdown layer comprises a sheet of materials selected such that the shutdown layer will melt at a temperature determined as the shutdown temperature of the electrical separator.

Claim 26 (Rejected): A process for producing the electrical separator for a lithium battery according to Claim 25, comprising:

preparing a suspension of inorganic nonelectroconductive particles in a sol;
applying the suspension to the surface and pores of a porous carrier to coat the carrier;
drying the coated carrier to form a porous inorganic nonelectroconductive coating on the surface and in the pores of the porous carrier; and

fixing on the porous inorganic nonelectroconductive coating a porous sheet shutdown layer;
wherein

the porous carrier is nonelectroconductive and has a porosity greater than 50%,
the inorganic nonelectroconductive particle comprises at least one oxide selected from the group consisting of an oxide of Al, an oxide of Si and an oxide of Zr,
the particles have an average particle size in the range from 0.5 to 10 μm ,
the sol comprises a hydrolysis product of a compound of Al, Si or Zr, and
the porous sheet shutdown layer comprises materials selected such that the shutdown layer will melt at a temperature determined as the shutdown temperature of the electrical separator.

IX. EVIDENCE APPENDIX

Kirk-Othmer Encyclopedia of Chemical Technology, Fifth Edition, Vol. 23, 2007, pages 76-79.

X. RELATED PROCEEDINGS APPENDIX

None

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 **WILEY-INTERSCIENCE**

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cavities, and a lower coefficient of thermal expansion, 0.2×10^{-6} cm/cm compared with 0.55×10^{-6} cm/cm. Optically transparent porous gel silica (Type VI) has a uv cutoff ranging from 250–300 nm. Type VI gel-silica optics have a density as low as 60% of Types I–V silica and can be impregnated with up to 30–40% by volume of a second phase of an optically active organic or inorganic compounds. Mechanical properties of the Type VI porous gel-silica monoliths have been determined (5) and related to topological and metric features.

4. Alumina Derived from Sol-Gel

Aluminum oxide [1344-28-1] (alumina), Al_2O_3 , has high technological value. Sol-gel processing of alumina has created novel applications and improved some of its properties. Products such as catalyst carriers, abrasives, fibers, films for electronic applications, aerogels, and membranes for molecular filtration have been developed on a laboratory scale based on sol-gel processing. Aluminum alkoxide hydrolysis has been studied for several decades to understand the diverse structures of aluminum hydroxides (46). In 1975, monolithic alumina samples derived from aluminum alkoxide were produced using four steps (13): hydrolysis of aluminum alkoxide, peptization of the hydrolyzed mixture, gel formation, and drying and pyrolysis (see ALUMINUM COMPOUNDS, ALUMINA).

4.1. Hydrolysis and Condensation Reactions of Aluminum Alkoxides. Aluminum alkoxides may be coordinatively unsaturated with three possible coordination numbers. Aluminum is less electronegative than silicon, causing it to be more electrophilic and thus less stable toward hydrolysis (21). These features are responsible for the greater rates of hydrolysis and condensation of aluminum alkoxides when compared to the rates of silicon alkoxide reactions. Hydrolysis and condensation reactions probably occur by nucleophilic addition, followed by proton transfer and elimination of either alcohol or water under neutral conditions. Both reactions are catalyzed by the addition of acid or base. When acids are added, they protonate organic or hydroxyl groups, creating reactive species and eliminating the requirement for proton transfer as an intermediate step. Bases deprotonate water or OH groups, leading to the formation of strong nucleophiles.

Condensation reactions tend to proceed along the reaction pathway that maximizes the hydrogen bonds of the aluminum hydroxides produced during hydrolysis (21). Because the pathway for condensation reactions is not random, formation of crystalline species is allowed. Aluminum alkoxides react rapidly with water, producing aluminum hydroxides having structure and shapes determined by the conditions in which hydrolysis was performed. The influence of hydrolysis temperature on the structure of the aluminum hydroxide formed has been shown (13). When high (80°C) hydrolysis temperatures are used, boehmite [1318-23-6] is formed as fibers and plates. When hydrolysis of the aluminum alkoxide is performed at low (room temperature) temperatures, an amorphous aluminum hydroxide is formed that has a higher residual content of organic radicals. The aging of this amorphous hydroxide at room temperature and in the mother liquor allows the beginning of a dissolution process followed by bayerite precipitation.

4.2. Peptization. Aggregation of small inorganic polymeric chains and clusters produced from hydrolysis and condensation reactions of aluminum alkoxides forms macroparticles and nonuniform aggregates. These aggregates that are broken during the peptization step effect the formation of a clear sol having a narrow distribution of particle size. Another mechanism associated with peptization is the production of surface charges on the colloids (47) that eventually leads to either gelation or dispersion. Variables influencing peptization of aluminum alkoxide sols are type and concentration of inorganic acids, temperature of hydrolysis, and the water/alkoxide ratio. Peptization of sols prepared at 90°C occurs when inorganic acids are added having acid/alkoxide molar ratios greater than 0.03. This leads to the formation of inorganic polymers having greater sizes and ramified chains. Otherwise, peptization only occurs in low temperature sols when additions of larger quantities of acid than those required to peptize mixtures hydrolyzed with hot water are provided. The resulting polymers have lower molecular weight (48).

4.3. Gelation. Mechanisms of gelation of alumina sols derived from alkoxides differ from gelation of silicon alkoxide sols. Whereas the sol-gel transition for silica sols is basically a consequence of interactions between long inorganic chains, the gel transition in alumina sols results from colloidal growth by dissolution and reprecipitation processes (Ostwald ripening), followed by formation of linkages between particles. These linkages are initialized by physical-chemical interactions between surface-charged colloids that eventually produce a three-dimensional network, formed by interconnected colloids. The initial contact points between colloids are responsible for neck formation by a coarsening process, followed by particle reshaping and densification. Gelation can be induced either by eliminating excess of water added during hydrolysis or by adding electrolytes to the peptized sol prepared in temperatures above 60°C that leads to sol flocculation.

The effects of both pH and temperature of aluminum alkoxide hydrolysis on gelation is shown in Figure 8. Addition of acid into the mixture hydrolyzed at

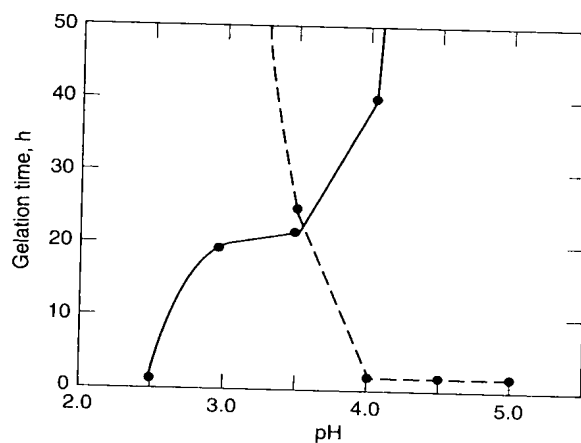


Fig. 8. Gelation behavior of alumina sols prepared from hydrolysis of aluminum isopropoxide at (—) 90°C and (---) room temperature (49).

90°C, and by consequence reduction of pH, reduces the gelation time of the samples, whereas in mixtures hydrolyzed at room temperature, acidic addition increases gelation time.

X-ray diffraction of alumina xerogels prepared at temperatures of hydrolysis higher than 50°C shows a pseudoboehmite phase. Xerogels prepared at room temperature have an amorphous structure (49). The presence of a large amount of residual organic groups, large content of acid, and large concentration of water stabilizes the amorphous structure of aluminum hydroxide. Structural analysis of gels can be used to explain the gelation behavior of sols prepared at different temperatures. Owing to the presence of a cleavage plane in pseudoboehmite colloids, edges of the colloidal plates have positive surface charges in acidic conditions, whereas faces that do not have primary broken bonds have negatively or less positively charged surfaces. Thus, face-edge attractions among colloids are increased with a reduction of pH, because pH reduction adds positive surface charges to the edges of plates. Mixtures hydrolyzed and peptized at room temperature produce amorphous colloids that do not have cleavage planes and are spherical in shape. Thus, surface charges are uniformly distributed. Addition of acid increases the positive surface charge density of colloids (increase in zeta potential), provoking a greater repulsion among the particles and extending the gelation time.

4.4. Drying of Gels. Drying of alumina gels prepared using high temperatures of hydrolysis consists of two steps: sol concentration and pore liquor removal. The rate of sol concentration can dictate some gel properties. High rates of sol concentration lead to less efficiency in packing of colloids.

Transparent monoliths can be prepared by drying high density gels (49,50). Control of initial conditions of sol preparation is essential to achieve success during the drying step.

4.5. Phase Transformations and Properties of Gels from Aluminum Alkoxide. Pure alumina xerogels, when submitted to heat treatments at 500 and 1100°C, give rise respectively to γ -alumina and α -alumina (47). This sequence of phase transformation is traditionally obtained for pure aluminum hydroxides. The effects of gel preparation conditions on the volumetric density and surface area are also compatible with the mechanisms of sol formation and gelation (49) described. Gels prepared at room temperature show a volumetric density much greater than gels prepared at 90°C as a result of both different magnitudes of capillary pressure and efficiency of packing. Moreover, the pH of mixtures hydrolyzed at high (>50°C) temperatures affects the gel structure, and a reduction in pH produces a reduction of the surface area of the gels prepared at 90°C. Short gelation times at progressively lower pHs (higher magnitude of face-edge attractions) allow the stabilization of a significant disorganization in the arrangement of the pseudoboehmite particles.

5. Economic Aspects

The sol-gel process can be utilized to yield products within a wide range of applications. Some of these applications include production of nanocomposites, films, fibers, porous and dense monoliths, and biomaterials.

Table 3. Markets for Sol-Gel Products^a

Markets	Year			Average annual growth rate, %
	1996	2001	2006	
United States	158.76	504	1600	26
rest of world	529	1064	2140	15

^aRef. 50.

The commercialization of sol-gel-derived products grew in the early to mid-1990s and is expected to grow faster in the twenty-first century (50).

Table 3 summarizes the value of markets for sol-gel products worldwide. Applications commanding the market as of 1995 were those related to abrasives (qv), coatings (qv), catalysts, and optical components, among others. A significant growth in the market from optical applications as well as from chemical sensors (qv) was expected for the late 1990s. Other products expected to emerge and have high importance are those related to biomedical applications and organic-inorganic hybrid composites.

6. Applications

6.1. Sol-Gel Processing of Thin Films. The sol-gel method enables the production of ceramic films having thickness from 10–1000 nm (see Thin films). The rheological characteristics of the sol allow the deposition of a film by several procedures: dip coating, spin coating, electrophoresis, thermophoresis, and settling (see COATING PROCESSES). Dip and spin coating are the most frequently used procedures. Dip coating can be divided into five stages (21): immersion, startup, deposition, drainage, and evaporation. The fluid mechanical boundary layer, which is pulled with the substrate, splits into two. The inner layer moves upward with the substrate, while the outer layer is returned to the bath. The thickness where the split occurs is responsible for the thickness of the film. Five events govern the split phenomenon (21) and consequently the thickness of the film: viscosity of the solution, force of gravity, resultant force of surface tension in the concavely curved meniscus, velocity of pulling, and reactivity between the sol particles and the substrate. A good correlation among viscosity, η ; substrate velocity, V ; and film thickness, h , can be given by the following equation:

$$h = c_1(\eta V / rg)^{1/2} \quad (9)$$

where c_1 is a constant, r is density, and g is gravitational acceleration. Thus low viscosities and low substrate withdrawal speed are necessary to produce thin films.

The spin coating process can be divided into four stages (51): deposition, spinup, spinoff, and evaporation. In the first stage, an excess of liquid is distributed along the surface that is to undergo deposition. The spinup stage is related to flow of liquid along all the surface, driven by centrifugal force. In the spinoff